

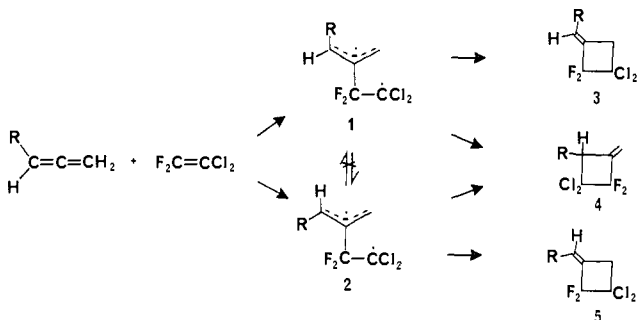
Detection and the Analysis of the Factors Affecting the Competition between Ring Closure, Internal Rotation, and Cleavage in Diradical Intermediates Formed in Allene Cycloaddition Reactions

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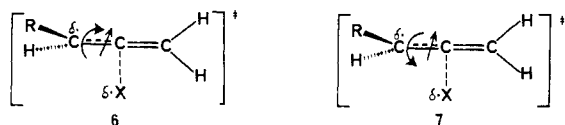
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Abstract: The cycloaddition reactions of the monoalkylallenes ethyl-, isopropyl-, and *tert*-butylallene and the dialkylallene 1,1-dimethylallene with diethyl fumarate (DEF) and maleate (DEM) have been investigated. The comparison of the chemo- and stereoselectivities observed in these reactions with those observed in the cycloaddition reactions with 1,1-dichloro-2,2-difluoroethene indicates that the reactions with DEF and DEM occur via two-step, diradical-intermediate processes. In the reactions with DEF *only* trans-diester cycloadducts are formed. In the reactions with DEM *both* cis- and trans-diester cycloadducts are formed, and isomerization of DEM to DEF is observed. The product distributions are interpreted in terms of preferred conformations of the diradical intermediates and the competition between ring closure, internal rotation, and cleavage reactions of the diradical intermediates.

Current studies in the author's laboratories are directed toward the understanding of the chemo- and stereoselectivities in concerted and nonconcerted cycloaddition reactions of substituted allenes. The reaction of substituted allenes with 1,1-dichloro-2,2-difluoroethene (1122) was chosen as a model for the two-step, diradical-intermediate cycloaddition process.¹ The reactions with monosubstituted allenes proceed cleanly at 160 °C (~12 h) to produce mixtures of the three cycloadducts **3–5** via the diradical intermediates **1** and **2**. As the size of the R group increases, the ratio of **3** to **5** increases. For example, when R is ethyl the ratio is 1.85:1.00, when R is isopropyl the ratio is 2.50:1.00, while when R is *tert*-butyl only **3** (and **4**) is formed. The observed stereo-



selectivities are interpreted in terms of steric interactions generated in the transition states for formation of **1** and **2**. In the formation of **1** the R group rotates *away* from the approaching reagent (transition-state **6**), while in the formation of **2** the R group rotates *toward* the approaching reagent (**7**) introducing greater steric strain in this transition state. A similar trend is observed in the cycloaddition reactions with unsymmetrically substituted 1,1-dialkylallenes.¹



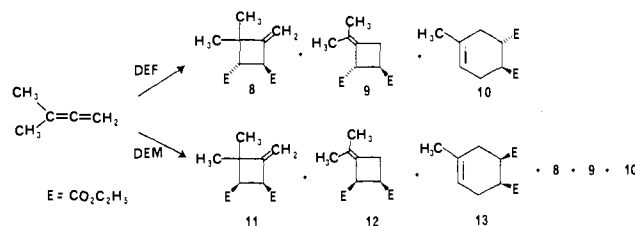
The comparison of the chemo- and stereoselectivities and relative reactivities observed in the cycloaddition reactions with 1122 with those observed in reactions with *N*-phenylmaleimide (NPMI) indicates that the latter reaction also proceeds via a two-step, diradical-intermediate pathway.² The results of these

two studies provided insights on the factors affecting diradical-intermediate formation and the competing ring-closure reactions. Because of the nature of 1122 and NPMI, information on possible cleavage and internal rotation processes of the diradical intermediates was not accessible.³ In an attempt to gain more detailed information on the competing reactions of diradical intermediates, we have now investigated the reactions of substituted allenes with diethyl fumarate (DEF) and maleate (DEM).

The cycloaddition reactions of 1,1-dimethylallene (DMA) with DEF and DEM have been studied previously by Kiefer and Okamura.⁴ The reaction of DMA with DEF was reported to occur with at least 99% stereospecificity, while the reaction of DMA and DEM resulted in the formation of 10–15% of trans-diester products. It was also noted that DEM underwent isomerization to a minor extent.⁵

Results

Reaction of DMA with DEF and DEM. The reaction of DMA with DEF in excess DEF as solvent at 160 °C for 5 days results in the formation of a mixture of *only* the trans-diester adducts **8–10** which were isolated by preparative GC. The reaction of DMA with DEM in DEM produces a *mixture* of the cis-diester adducts **11–13** and the trans-diester adducts **8–10**. Some isom-



erization of DEM to DEF occurs during the reaction with DMA. However, when DEM was heated at 160 °C for 5 days in the absence of DMA, *no* isomerization of DEM was detected. The cycloadducts were similarly shown to be configurationally stable at 160 °C for 5 days.

The trans and cis relationships between the ester functions in **8** and **9**, and **11** and **12**, are indicated by the relative magnitudes

(3) For an excellent review of the chemistry of diradical intermediates derived in the gas-phase thermolysis of methylenecyclobutanes and cycloaddition reactions, see: Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; pp 90–94.

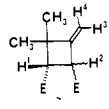
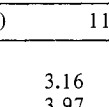
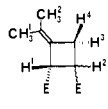
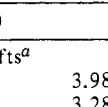
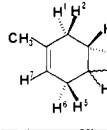
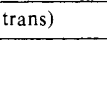
(4) Kiefer, E. F.; Okamura, M. Y. *J. Am. Chem. Soc.* **1968**, *90*, 4187.

(5) Although these results were originally interpreted in terms of concerted cycloaddition processes, later studies on the generation and reactions of 2,2'-bis(1,1-dimethylallyl) diradical⁶ (the diradical intermediate derived in the cyclodimerization of DMA) led to the conclusion that allene cycloaddition reactions occur via nonconcerted processes.

(1) Pasto, D. J.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3670.

(2) Pasto, D. J.; Heid, P. F.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3676.

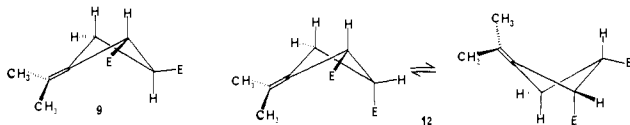
Table I. NMR Parameters of 8-13

												
	8 (trans)	11 (cis)	9 (trans)	12 (cis)	10 (trans)	13 (cis)						
Chemical Shifts ^a												
H ¹	3.24	3.16	4.16 (ax)	3.98 (ax)	H ¹	2.28	2.39					
H ²	4.14	3.97	3.40	3.28 (eq)	H ²	2.15	2.18					
H ³	4.92	4.97	2.96 (eq)	3.19 (eq)	H ³	2.87	2.94					
H ⁴	5.05	5.22	2.76 (ax)	2.78 (ax)	H ⁴	2.77	2.94					
CH ₃	1.09, 1.27	1.18, 1.35	1.51 ⁽¹⁾ , 1.57 ⁽²⁾	1.33; 1.58 ²	H ⁵	2.15	2.25					
E (CH ₂)	4.19 (m)	4.14, 4.16, ^b 4.17	4.16, 4.19 ^b	4.15, 4.14, ^b 4.15	H ⁶	2.39	2.45					
(CH ₃)	1.09, 1.27	1.26, 1.27		1.23, 1.23	H ⁷	5.39	5.31					
					CH ₃	1.63	1.62					
					E-CH ₂ -	4.143; 4.147, ^b 4.155	4.07 (m)					
					-CH ₃ -	1.26, 1.25	1.18, 1.19					
Coupling Constants												
1, 2	8.44	9.44	1, 2	6.17	1, 2	16.0	17.0					
2, 3	3.19	2.93	1, 3	3.27	1, 3	10.79	6.00					
2, 4	2.70	2.56	1, CH ₃ ¹	1.0	2, 3	5.67	4.87					
E (CH ₂ -CH ₃)	7.14	7.11, 7.14	1, CH ₃ ²	1.45	3, 4	10.85	c					
			2, 3	10.19	4, 5	10.85	c					
			2, 4	6.17	4, 6	5.34	4.7					
			3, 4	14.71	5, 6	16.0	17.8					
			3(4), CH ₃ ¹	1.73								
			3(4), CH ₃ ²	1.53								
			E (-CH ₂ -CH ₃)	7.11, 7.12	7.08, 7.09							

^a Recorded in CDCl₃ solution on a Nicolet NB-300 spectrometer. ^b Diastereotopic methylene hydrogens. ^c Could not be resolved. ^d The *cis*-13 could not be completely separated from *trans*-10 by preparative GC. The NMR parameters of 13 were determined from a sample of pure 13 prepared by the direct reaction of DEM with isoprene.

of coupling constants between H¹ and H² obtained from the complete analysis of the 300-MHz NMR spectra⁷ (see Table I). In the *trans* adducts the H¹-H² coupling constants are smaller than those in the *cis* adducts by 1-2 Hz. A model of a slightly puckered methylenecyclobutane ring shows that the dihedral angle between *cis*-related hydrogens is considerably smaller than that between *trans*-related hydrogens.⁸ In **9** and **12** the assignment of the methyl resonances is based on the relative magnitudes of the homoallylic, long-range coupling constants with H¹ and H³- (H⁴); the (*E*)-⁵*J* being greater than the (*Z*)-⁵*J*.⁹

The presence of observable cross-ring, long-range coupling between H¹ and the pseudoequatorial H³ defines the dominant conformations of **9** and **12**. The values of *J*_{1,3} of ~3 Hz (*J*_{1,4} is apparently very small and could not be observed) suggest an axial-equatorial relationship.¹⁰ These data, in conjunction with the other coupling constant data, define the conformations as shown below. In **9**, both ester functions are pseudoequatorial.



In **12**, the ester function at C₂ must be pseudoequatorial and that at C₃ pseudoaxial, despite the apparent steric interaction between CH₃¹ and the adjacent ester function. The lack of an axial hydrogen at C₁ does not disfavor the axial orientation at C₃ to the extent observed in a cyclobutane system.

(6) Levek, T. J.; Kiefer, E. F. *J. Am. Chem. Soc.* **1976**, *98*, 1875.

(7) The original assignment of the stereochemistry of the adducts⁴ was based on the assumption that DEF should produce predominantly cycloadducts with *trans* carboethoxy groups regardless of the mechanism of the reaction. Apparently, the 60-MHz NMR spectra were not sufficiently resolved to determine all of the coupling constants.

(8) The trends in the relative magnitudes of the various coupling constants reported here are fully consistent with the trends reported for the more highly puckered cyclobutanol (Wiberg, K. B.; Barth, D. E. *J. Am. Chem. Soc.* **1969**, *91*, 5124).

(9) Sternhall, S. *Rev. Pure Appl. Chem.* **1964**, *14*, 15.

(10) See the reference in 8.

Table II. Yields of Adducts from DMA with DEF and DEM

dienophile ^a	8	9	10	11	12	13	
DEM	5.9	8.8	16.8	15.0	33.4	20.1	
DEF	9.1	69.9	21.0				
DEF + DMA							
solvent	temp, °C	8	9	10			
toluene	160	17.5	75.7	6.8			
	180	10.8	68.5	20.7			
	200	4.8	35.1	60.1			
anisole	160	9.2	54.8	35.9			
	180	7.7	43.8	48.5			
	200	4.3	26.6	69.1			
chlorobenzene	160	7.4	61.0	31.6			
	180	9.3	47.2	43.5			
	200	3.0	32.4	64.6			
DEM + DMA							
solvent	temp, °C	8	9	10	11	12	13
toluene	160	8.5	9.2	5.1	18.0	47.0	11.8
	180	9.4	29.3	33.5	1.0	21.1	5.7
	200	3.2	20.3	59.3	1.2	6.0	6.4
anisole	180	2.4	7.6	58.9	0.5	10.1	20.5
	200	1.2	6.8	75.1	1.5	4.6	11.0
chlorobenzene	180	3.9	15.0	57.5	0.2	11.1	12.3
	200	2.6	13.9	64.2	0.9	7.6	10.8

^a In excess DEM or DEF as solvent.

The cycloadducts **10** and **13** are formally those derived from isoprene¹¹ with DEF and DEM. The analysis of the 300-MHz

(11) The isoprene is formed from DMA by a [1,3]-sigmatropic rearrangement. The glass tubes used for the reactions were carefully washed with acid and base and then repeatedly washed with water, similar to the procedures used previously in the 1122 and NPMI reactions in which no rearrangement was observed. The cycloaddition reactions of DMA with DEF and DEM occur much more slowly than with 1122 and NPMI, allowing the [1,3]-sigmatropic rearrangement to become competitive. A similar [1,3]-sigmatropic rearrangement has been noted previously in the reactions of tetramethylallene with DEF and DEM.⁴

Table III. Relative Yields of 8 and 9 as a Function of Temperature in Toluene

temp, °C	DEF ^a		DEM	
	8	9	8	9
160 ^a	11.5	88.5	40.4	59.6
160	13.8	86.2	48.0	52.0
180	13.2	86.8	24.3	75.7
200	11.9	88.1	13.6	86.4

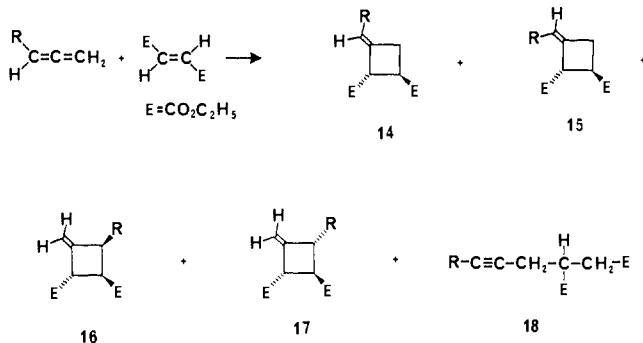
^a In neat reagent.

NMR spectra allowed assignment of the stereochemistry, which was confirmed by their independent synthesis.

The yields of the adducts derived in the reactions of DMA with DEF and DEM, in DEF and DEM respectively, are given in Table II.¹²

The reactions of DMA with DEF and DEM were also carried out in toluene, anisole, and chlorobenzene solution at 160, 180, and 200 °C. The yields of the adducts are given in Table II. The relative yields of 8:9 derived in the reactions of DMA with DEF and DEM in toluene as a function of temperature are given in Table III.

Reactions of Monoalkylallenes with DEF. The reactions of the monoalkylallenes ethyl-, isopropyl, and *tert*-butylallene with DEF in excess DEF as solvent at 160 °C for 10–12 days produce mixtures of only the *trans*-diester adducts 14–17 and the ene-product 18, which could be partially separated by preparative GC (see Experimental Section). In cases where complete separation



could not be achieved, partial peak collection and NMR spectral subtraction techniques were used, or the NMR spectra of the mixtures were analyzed directly. The NMR spectral data for 14–18 appear in Table IV. The yields of 14–18 are given in Table V.

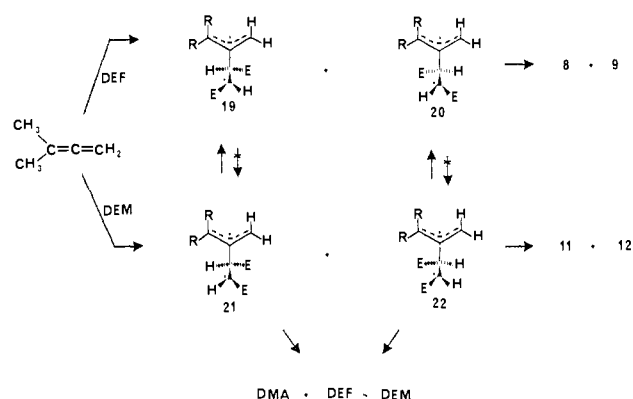
The assignments of (*E*) and (*Z*) stereochemistry about the exocyclic double bond have been made on the basis of well-established trends in the relative magnitudes of (*E*)- and (*Z*)-allylic and -homoallylic coupling constants^{1,9} and long-range shielding effects on H¹, H², and the alkyl (R) groups.¹

The assignments of the stereochemistry in 16 and 17 have been made on the basis of the relative magnitudes of the vicinal and cross-ring, H¹-H³ coupling constants and the higher-field position of pseudoaxial hydrogens.¹⁰ In cyclobutane, the axial-equatorial H¹-H³ coupling constants in 16 are larger than the axial-axial coupling constants in 17.¹⁰

The structures of the ene-products 18 are readily assigned on the basis of their NMR spectra. Similar ene-type products are formed in the reactions of monoalkylallenes with *N*-phenylmaleimide.²

Reaction of *tert*-Butylallene with DEM. The reaction of *tert*-butylallene with DEM produces a mixture of products of which the *trans*-diester adducts 14, 16, and 17 comprised ~90% of the cycloadduct mixture (see Table V). Extensive isomerization

Scheme I



(6%) of the DEM to DEF was evident at the end of the reaction. In addition to the three *tert*-Bu peaks representing 14, 16, and 17, three additional, weak *tert*-Bu singlets were present in the NMR spectrum of the crude reaction mixture. It was not possible, however, to isolate these fractions by preparative GC, and the assignment of the three weak *tert*-Bu signals to *cis*-diester cycloadducts is purely speculative. The relative yields of the *trans*-diester adducts and 18 are given in Table V.

Reaction mixtures derived from reactions of ethyl- and isopropylallene with DEM proved impossible to separate, and these reactions were not further explored.

Discussion

The results described in the foregoing section are readily rationalized in terms of a diradical-intermediate mechanism in which internal rotation and cleavage reactions of the diradical intermediate compete with the ring-closure reactions. A comparison of the trend in the preferred stereoselectivity about the exocyclic double bond in 14 and 15 and the general product distributions, derived in the reactions of the monoalkylallenes with DEF (Table V), with those observed in the cycloaddition reactions with 1122' and NPMI² indicates that the reactions with DEF proceed via diradical-intermediate mechanisms. In particular, it should be noticed that as the size of the R group increases, the yield of the (*Z*)-isomer 15 decreases, none of this adduct being formed when R is *tert*-butyl. The reasons for this trend have been discussed in the introduction of this paper. The lack of an apparent solvent effect on the product distributions is consistent with a diradical-intermediate mechanism.

It is important to note that the *trans,cis*-isomer 16, in which the R group is *cis* to the ester function, is formed to a significantly greater extent than is the *trans,trans*-isomer 17. This is the case even when R is *tert*-butyl in which there will be considerably more steric repulsion in the transition state for ring closure than in the cases when R is ethyl or isopropyl, or than that in the transition states for ring closure to form 17. The reasons for these trends will be discussed in more detail later.

Reaction of DMA with DEF and DEM. It is important to note that in the reaction of DMA with DEF *only* *trans*-diester products 8–10 are formed.¹³ In contrast, the reaction of DMA with DEM produces *both* *cis*- and *trans*-diester products.⁴ Furthermore, isomerization of DEM to DEF occurs in the presence of DMA as evidenced by an increase in the amount of DEF present in the DEM after the reaction, as well as by the formation of 11 which can only be formed by the direct cycloaddition of isoprene¹¹ with *free* DEF. It is also instructive to compare the 8:9 ratios formed in neat DEF and DEM at 160 °C and the temperature dependence on the 8:9 ratio in toluene solution (see Table III). In DEF this ratio is 11.5:88.5; while in DEM the ratio is 40.4:59.6. At 160 °C in toluene the ratios are similar to those in neat DEF and DEM

(12) Mass spectral analysis of the crude reaction mixtures indicated the presence of small amounts of 2:1 adducts, possibly of the same type isolated in the reaction of DMA with NPMI.² The NMR spectra of the reaction mixtures indicated that the 2:1 adducts were present in <5%, and no attempt was made to isolate these adducts.

(13) The *cis*- and *trans*-diester adducts 11 and 12, and 8 and 9, derived from DMA are well resolved by analytical GC. The yields of the *cis*-diester adducts formed in the reaction of DMA with DEF must be less than 0.1%, if they are formed at all.

Table IV. NMR Parameters of 14-18^a

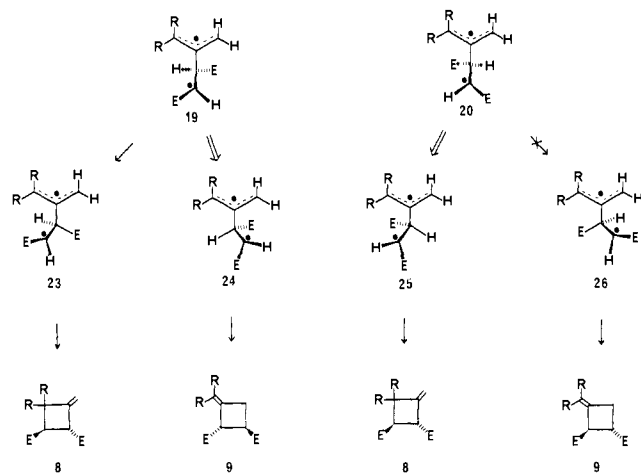
	R =			R =								
	-CH ₂ CH ₃	-CH(CH ₃) ₂	-C(CH ₃) ₃	-CH ₂ CH ₃	-CH(CH ₃) ₂	-C(CH ₃) ₃						
 14							(-CH ₃)	0.93	0.88, 0.93 ^b	0.98		
	E (-CH ₂ -)	4.17, 4.18; ^b 4.19	4.18 (m)	4.18 (m)								
	(-CH ₃ -)	1.28, 1.29	1.28	1.291, 1.294								
Chemical Shifts												
H ¹	4.00	3.99	3.98									
H ²	3.52	3.52	3.55									
H ³	2.93	2.94	3.13									
H ⁴	2.82	2.85	3.04									
H ⁵	5.46	5.32	5.38									
R (-CH ₂ -)	1.92, 1.93 ^b	2.29 (CH)										
(-CH ₃)	0.96	0.94, 0.96	1.02									
E (-CH ₂ -)	4.22 (m)	4.172, 4.176; ^b 4.181, 4.187 ^b	4.15, 4.21; ^b 4.17									
(-CH ₃)	1.27	1.29	1.29; 1.27									
Coupling Constants												
1, 2	7.33	7.49	7.68									
1, 3		2.7	3.02									
1, 4		0.74	0.84									
1, 5	2.85	2.6	2.42									
1, R	1.38	1.73										
2, 3	8.00	9.89	9.80									
2, 4	7.71	8.03	8.10									
3, 4	15.53	15.34	15.92									
3(4), 5	2.47	2.7	(3, 5) 2.47; (4, 5) 2.79									
3(4), R	1.16											
5, R	7.38	8.9										
E (CH ₂ , CH ₃)	7.33	7.13	7.02, 7.02									
 15							(-CH ₃)	0.93	0.88, 0.93 ^b	0.98		
	E (-CH ₂ -)	4.17, 4.18; ^b 4.19	4.18 (m)	4.18 (m)								
	(-CH ₃ -)	1.28, 1.29	1.28	1.291, 1.294								
Chemical Shifts												
H ¹	4.03	4.03	^c									
H ²	3.48	3.48										
H ³	2.98	2.99										
H ⁴	2.84	2.83										
H ⁵	5.28	5.11										
R (-CH ₂ -)	2.00, 2.01 ^b	2.48 (CH)										
(-CH ₃)	0.93	0.90, 0.94										
E (-CH ₂ -)	4.18, 4.19, 4.20 ^b	4.18, 4.21; ^b 4.17										
(-CH ₃)	1.267, 1.271	1.273, 1.297										
Coupling Constants												
1, 2	6.23	6.35										
1, 3	3.0	3.16										
1, 4												
1, 5	2.32	2.56										
1, R	1.94											
2, 3	10.15	10.19										
2, 4	6.94	6.93										
3, 4		15.47										
3(4), 5	2.67	2.24										
3(4), R	1.44											
5, R	7.50	9.27										
R; CH ₂ , CH ₃	7.40											
E; CH ₂ , CH ₃	6.35, 6.31	7.21, 7.22										
 16							(-CH ₃)	0.93	0.88, 0.93 ^b	0.98		
	E (-CH ₂ -)	4.17, 4.18; ^b 4.19	4.18 (m)	4.18 (m)								
	(-CH ₃ -)	1.28, 1.29	1.28	1.291, 1.294								
Chemical Shifts												
H ¹	4.18	4.09	4.13									
H ²	3.61	3.59	3.58									
H ³	3.11	3.00	3.16									
H ⁴	4.96	4.97	4.99									
H ⁵	5.14	5.19	5.21									
R (-CH ₂ -)	1.47, 1.57 ^b	1.99 (CH)										
 17							(-CH ₃)	0.93	0.88, 0.93 ^b	0.98		
	E (-CH ₂ -)	4.17, 4.18; ^b 4.19	4.18 (m)	4.18 (m)								
	(-CH ₃ -)	1.28, 1.29	1.28	1.291, 1.294								
Chemical Shifts												
H ¹	3.98	3.91	3.86									
H ²	3.14	3.25	3.31									
H ³	3.00	2.93	<i>d</i>									
H ⁴	4.96	5.01	5.05									
H ⁵	5.10	5.14	5.19									
R (-CH ₂ -)	1.54, 1.71	1.86 (CH)	<i>d</i>									
(-CH ₃)	0.97	0.93, 0.99 ^b	0.95									
E (-CH ₂ -)	4.18 (m)	4.18 (m)	<i>d</i>									
(-CH ₃)	1.28, 1.29	1.27, 1.29	1.287, 1.292									
Coupling Constants												
1, 2	7.89	7.80	7.64									
1, 3	1.12	0.79	<i>d</i>									
1, 4	2.43	2.56	2.60									
1, 5	3.10	3.21	3.35									
2, 3	8.22	8.10	8.20									
3, 4	3.22	3.31	3.05									
3, 5	2.60	3.07	2.87									
3, R	7.20	6.76	<i>d</i>									
4, 5	<i>d</i>	0.87	0.82									
R; H-C-H	14.57		<i>d</i>									
R; CH, CH ₃	7.20	6.76	<i>d</i>									
E; CH ₂ , CH ₃	6.96, 7.07	7.08, 7.09	<i>d</i>									
 18							(-CH ₃)	0.93	0.88, 0.93 ^b	0.98		
	E (-CH ₂ -)	4.17, 4.18; ^b 4.19	4.18 (m)	4.18 (m)								
	(-CH ₃ -)	1.28, 1.29	1.28	1.291, 1.294								
Chemical Shifts												
H ¹	2.51	2.51	2.49									
H ²	2.53	2.53	2.52									
H ³	2.97	2.97	2.98									
H ⁴	2.78	2.66	2.64									
H ⁵	2.81	2.80	2.80									
R (-CH ₂ -)	2.15	2.54 (CH)										
(-CH ₃)	1.14	1.13	1.18									
E (-CH ₂ -)	4.18	4.15, 4.17	4.17, 4.18; ^b 4.15									
(-CH ₃)	1.28	1.27	1.268, 1.271									
Coupling Constants												
1, 2		16.70	16.02									
1, 3	4.7	5.35	5.62									
2, 3	5.3	8.63	7.40									
3, 4	5.4	7.42	5.28									
3, 5	8.5	8.15	8.67									
4, 5	16.6	17.20	16.76									
4(5), R	2.53	1.42, 2.77										
R	7.56	6.73										
E; CH ₂ , CH ₃	7.18	7.14	7.13, 7.14									

^a Recorded in CDCl₃ solution. ^b Diastereotopic methylene hydrogens. ^c Cycloadduct is not found. ^d Could not be resolved.

Table V. Relative Yields of Adducts 14-18 Derived from Monoalkylallenes with DEF and DEM

R	electrophile	14	15	16	17	18
-CH ₂ CH ₃	DEF	28.8	10.2	40.8	9.6	10.6
-CH(CH ₃) ₂	DEF	30.0	6.7	21.2	11.7	30.4
-C(CH ₃) ₂	DEF	38.5		21.6	3.2	36.7
-C(CH ₃) ₃	DEM	22		11	16	51

Scheme II



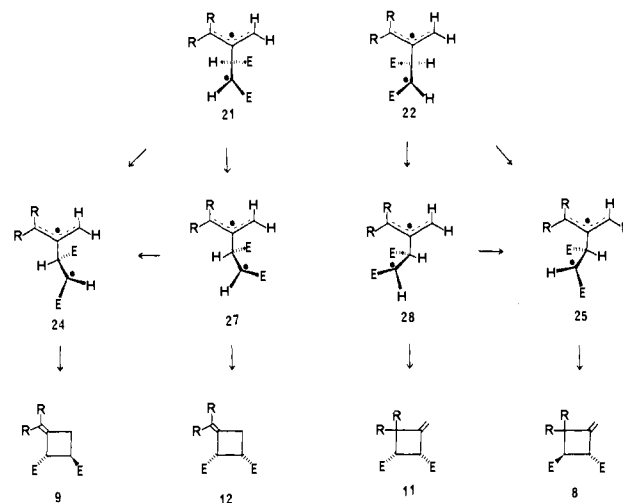
at the same temperature. However, as the temperature increases, the 8:9 ratio derived with DEM approaches that derived with DEF.

These results can be accounted for as shown in Scheme I in which the diradical intermediates derived from DMA and DEM (21 and 22) undergo internal rotation to generate the diradical intermediates derived from DMA and DEF (19 and 20) as well as cleavage to form DEF (and presumably DEM). The diradical intermediates derived from DMA and DEF do not undergo rotation to those derived from DMA and DEM. Whether or not cleavage occurs in the diradical intermediates derived from DMA and DEF cannot be ascertained with the presently available data.

The conformations of 19-22 correspond to those earlier suggested for the diradical intermediates formed in the reaction of optically active 2,3-pentadiene with acrylonitrile.¹⁴ In 19 and 20 the large ester functions are antiperiplanar, or nearly so as initially formed, representing the lowest energy conformations. In 21 and 22 derived from DEM the ester groups must be initially eclipsed. Such conformations must represent energy maxima, and must undergo rotational relaxation to form synclinal-type conformations or undergo further rotation to form 19 and 20. The trend toward identical 8:9 ratios from DEF and DEM at higher temperatures suggests that a minimum-energy conformation close to the eclipsed conformations must exist, but the barriers to rotation and cleavage must be rather small, and more rotation and cleavage occurs at the higher temperatures with 21 and 22.

In order to account for the observed product distributions observed in the reactions with the monoalkylallenes, in particular the preference for the formation of 16 over 17, slight modifications in the conformations of 19-22 are required. In 19-22 the newly formed C-C bond of the DEF and DEM has been arbitrarily oriented perpendicular to the plane of the allyl-radical portions of 19-22. These conformations, however, do not appear to represent energy minima. Slight rotations about the newly formed C-C bond result in lower energy conformations (see Scheme II) in which either the C-H (24 and 25) or the C-ester bond (23 and 26) is in the plane of the allyl radical. Of these conformations, 24 and 25 should be of lower energy than 23 and 26, due to smaller 1,3-diaxial-type interactions, and should be favored (indicated by \Rightarrow) in Scheme II). In 23-26 the H-C-CO₂C₂H₅ groups are tilted toward one of the ends of the allyl radical in an excellent position to undergo ring closure.

Scheme III



An analysis of the steric interactions in the transition states for diradical-intermediate formation suggests that 19 (or 23 and 24) should be favored over 20 (or 25 and 26). Thus, overall, cycloadduct 9 would be expected to be the dominant cycloadduct formed. This is consistent with the observed results.

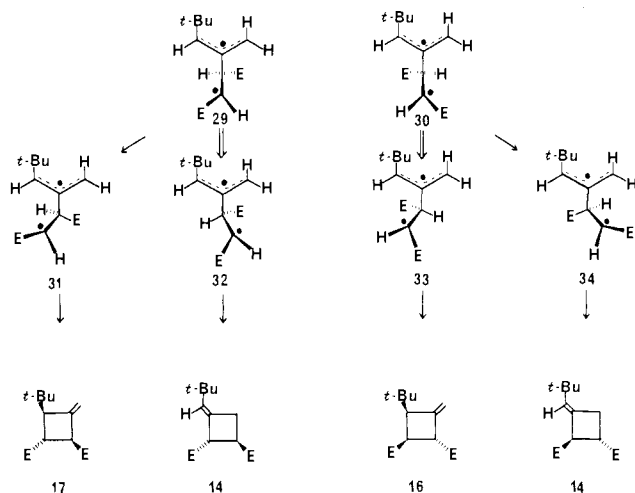
A similar analysis of the rotational processes in the diradical intermediates 21 and 22 formed in the reaction of DMA with DEM is shown in Scheme III. In this scheme only the more favored rotational relaxations of 21 and 22 to 27 and 28 are shown, which undergo subsequent ring closure to form the cis-diester products 11 and 12. In 21 and 22 the ester functions are eclipsed or synclinal, which are much higher energy conformations than those in which the ester functions are antiperiplanar or anticlinal. Thus, the rotation barriers from 27 to 24, and 28 to 25, must be relatively small, providing for facile conformational isomerization. (It is not possible to ascertain whether the isomerization to 24 and 25 occurs in a single step or via a two-step process.) The substantially lower 8:9 product ratio observed in the reaction of DMA with DEM, compared to that observed in the reaction of DMA with DEF (see Table III), indicates that 28 undergoes rotation to form 25 much more rapidly than does 27 to form 24. (It must be remembered that 21 must be formed in preference to 22.) This is not unexpected in that the sum of the repulsive steric interactions in 28 must be greater than that in 27, thus raising the energy of the diradical intermediate and increasing its reactivity. At higher temperatures the tendency toward rotational conformational equilibrium will increase, as will also the isomerization of DEM to DEF via cleavage of the diradical intermediates, resulting in a convergence of the 8:9 product ratios in the reactions of DMA with DEF and DEM.

In summary, in the reactions of DMA with DEM, higher-energy diradical intermediates are formed compared to those from the reaction of DMA with DEF. The product distributions suggest that the energy barriers to ring closure are approximately the same in the two reactions but that the energy barrier to rotation is significantly reduced in the eclipsed or synclinal diradicals allowing internal rotation to compete effectively with ring closure. It also appears that the energy barrier for cleavage is similarly affected.

Reaction of Monoalkylallenes with DEF. Three trends in the product distributions derived from the reactions of the monoalkylallenes with DEF are noteworthy. The first is the decrease in the yield of 15 relative to 14 as the size of the alkyl group increases. This strongly indicates that a two-step, diradical mechanism is operative.¹ The second trend is the increase in the yield of the terminal-attack, ene-product 18 as the size of the alkyl group increases. Similar trends have been observed in the reactions with NPMI² and benzenethiol¹⁵—reactions which proceed via diradical and radical intermediates, respectively. This change in

(14) Baldwin, J. E.; Roy, U. V. *Chem. Commun.* 1969, 1225.(15) Pasto, D. J.; Warren, S. E.; Morrison, M. A. *J. Org. Chem.* 1981, 46, 2837.

Scheme IV

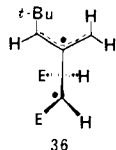
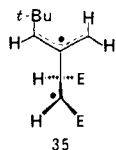


product distribution has been attributed to increased steric effects inhibiting attack at C_2 .

The third trend in the product distribution data is the predominant formation of the trans,cis-cycloadduct **16** over the trans,trans-adduct **17**, particularly when R is *tert*-butyl. Models indicate that the transition states for formation of **16** are much more sterically congested than those for formation of **17**. When R is *tert*-butyl, the lack of formation of **15** indicates that the only diradical intermediates formed are **29** and **30** (see Scheme IV). Intermediate **29** will undergo predominant rotational relaxation (indicated by \rightleftharpoons) to form **32** which undergoes ring closure to form **14**. The minor rotational pathway from **29** will form **31** which closes to form the minor trans,trans-adduct **17**. Intermediate **30** will undergo predominant rotational relaxation to form **33**. If ring closure occurs faster than any other rotational process in **33**, ring closure from **33** will form only the trans,cis-adduct **16**. The minor rotational pathway in **30** will form **34** and ultimately **14**. Thus, the conformational preferences in the diradical intermediates with antiperiplanar or anticlinal ester functions determine the product distributions.

The overall product distribution obtained with *tert*-butylallene suggests that the ratio of the stereoisomeric diradicals **29:30** is smaller than that for **19:20** in the reaction of DEF with DMA. This is consistent with less steric congestion in the transition states of the reactions of the monoalkylallenes with DEF.

Reaction of *tert*-Butylallene with DEM. GC and NMR analysis of the reaction mixture derived from *tert*-butylallene and DEM shows that approximately 90% of the cycloadducts have the esters in a trans relationship. The extent of crossover from cis to trans is much greater than that observed in the reaction of DEM with DMA. Extensive isomerization of DEM to DEF occurs, and the amount of the ene product has increased. These results indicate that rotation within and cleavage of the diradical intermediates **35** and **36** occurs more extensively than in the other diradical



intermediates formed in this study. Intermediates **35** and **36** must be of much higher relative energy than the other diradical intermediates due to a summation of the eclipsing strain energy of the ester functions and that present in the (*Z*)-1-*tert*-butylallyl radical.

Summary

The present results have provided interesting insights concerning the factors governing the competition between ring closure, internal rotation, and cleavage in diradicals. The energy barriers to ring closure appear to remain fairly constant regardless of the strain energy present in the diradical. In contrast, the energy barriers to rotation and cleavage appear to decrease with increasing strain energy.

Although in this study only the effects of increasing the energy of the diradical intermediate have been observed, it should be possible to stabilize either, or both, radical centers thereby lowering the energy of the diradical intermediate. It will be of interest to see what affects this will have on the competition between the various reactions of the diradical intermediate.

Experimental

General Procedure for the Cycloaddition Reactions. All cycloaddition reactions were carried out in sealed tubes at the temperatures indicated. The glass tubes were prepared by first washing with 1 N aqueous hydrochloric acid and then 1 N aqueous sodium hydroxide and then extensively with distilled water and finally with methanol. The tubes were then dried at 110 °C.

To 0.5 mL of solvent or neat DEF or DEM in the glass tube was added 1.0 mmol of the allene and 1.1 mmol of DEF or DEM (when not using DEF or DEM). The contents of the tubes were triply freeze-degassed, and the tube was sealed under reduced pressure. The sealed tube was then heated in a sand bath at the indicated temperature for the designated time (determined by earlier trial runs), after which the contents of the tubes were removed, and the solvent was removed under reduced pressure. The product mixtures were separated by preparative GC on 8–12 ft \times $\frac{1}{4}$ in. Carbowax 20M on Chromosorb P columns at 180–220 °C. The elemental compositions of all adducts have been determined by high-resolution mass spectrometry. The NMR spectra of the adducts were recorded in $CDCl_3$ solution on a Nicolet NB-300 spectrometer with FT techniques.

Ethylallene (1,2-Pentadiene) with DEF. The following elution sequence was observed on preparative GC separation: peak 1, **17**; peak 2, mixture of **15** and **16**; peak 3, **14**; peak 4, **18**.

Isopropylallene (4-Methyl-1,2-pentadiene) with DEF: peak 1, mixture of **15** and **17**; peak 2, mixture of **14** and **16**; peak 3, **18**.

***tert*-Butylallene (4,4-Dimethyl-1,2-pentadiene) with DEF and DEM:** peak 1, mixture of **17** and **18**; peak 2, **14**; peak 3, **16**.

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Registry No. **8**, 87902-69-0; **9**, 87902-70-3; **10**, 87902-71-4; **11**, 87902-72-5; **12**, 87902-73-6; **13**, 87902-74-7; **14** (R = CH_2CH_3), 87902-75-8; **14** (R = $CH(CH_3)_2$), 87902-76-9; **14** (R = $C(CH_3)_3$), 87902-77-0; **15** (R = CH_2CH_3), 87936-49-0; **15** (R = $CH(CH_3)_2$), 87936-50-3; **15** (R = $C(CH_3)_3$), 87936-51-4; **16** (R = CH_2CH_3), 87902-78-1; **16** (R = $CH(CH_3)_2$), 87902-79-2; **16** (R = $C(CH_3)_3$), 87902-80-5; **17** (R = CH_2CH_3), 87936-52-5; **17** (R = $CH(CH_3)_2$), 87936-53-6; **17** (R = $C(CH_3)_3$), 87936-54-7; **18** (R = CH_2CH_3), 87902-81-6; **18** (R = $CH(CH_3)_2$), 87902-82-7; **18** (R = $C(CH_3)_3$), 87902-83-8; DEF, 623-91-6; DEM, 141-05-9; DMA, 598-25-4; ethylallene, 591-95-7; isopropylallene, 13643-05-5; *tert*-butylallene, 26981-77-1.